Fire and Water: Assessing Drinking Water Contamination After a Major Wildfire

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ABSTRACT: We investigated patterns of volatile organic compound (VOC) contamination in drinking water systems affected by the California 2018 Camp Fire. We performed spatial analysis of over 5000 water samples collected over a 17 month period by a local water utility, sampled tap water for VOCs in approximately 10% (N = 136) of standing homes, and conducted additional nontargeted chemical analysis of 10 samples. Benzene contamination was present in 29% of service connections to destroyed structures and 2% of service connections to standing homes. A spatial pattern was apparent. Tap water in standing homes 11 months after the fire contained low concentrations of benzene in 1% of samples, but methylene chloride was present in 19% of samples, including several above regulatory limits. Elevated methylene chloride was associated

Burned Water Meter

- Benzene Detection
- Non-Detection

Paradise, CA, USA

with greater distance from the water meter to the tap, longer stagnation time, and the presence of a destroyed structure on the service connection; it was inversely associated with certain trihalomethanes. Nontargeted analysis identified multiple combustion byproducts in the water at 2/10 homes. Our findings support the hypothesis that pyrolysis and smoke intrusion from depressurization contributed to the benzene contamination. Further research is needed to test the hypothesis that methylene chloride may be generated from the dehalogenation of disinfection byproducts stagnating in galvanized iron pipes.

KEYWORDS: *wildfire, benzene, methylene chloride, volatile organic compounds (VOCs), drinking water, nontargeted analysis, California*
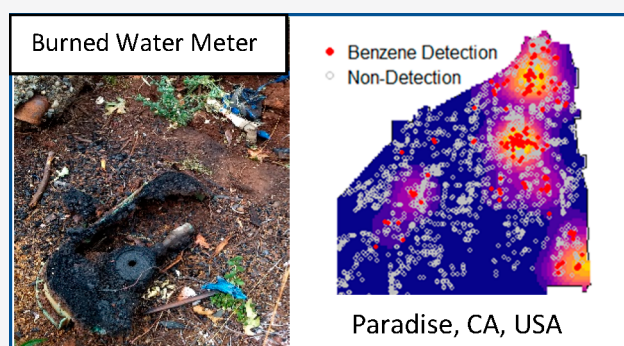
■ INTRODUCTION

Massive wildfires tore through towns in California in recent years. The magnitude and destruction from these fires is unprecedented, with loss of life and property, air quality impacts lasting weeks, large-scale generation of hazardous and municipal waste, and disruption of the social fabric. A new and unanticipated problem arose after recent California fires: the contamination of drinking water systems by volatile organic compounds (VOCs). Benzene and other VOC contamination in tap water was first reported after the Tubbs Fire in Santa Rosa, California in 2017.[1] The water contamination in Santa Rosa affected mostly vacant lots and only 13 standing homes. In contrast, after the Camp Fire in November 2018, approximately 1700 homes were still standing in the burn zone.

The Camp Fire destroyed about 14 000 homes; at least 86 people lost their lives when the towns of Paradise, Concow, and Magalia burned over a period of a few hours. Although the water treatment facilities and pumps continued to operate during the fire, there was a loss of system pressure in most areas due to large outflows of water from firefighting activities and broken pipes. In the weeks after the fire, the California Division of Drinking Water and local water utilities tested for VOCs, on the basis of the experience in Santa Rosa. The

agencies found no VOCs in the source water or at the treatment plant but detected benzene and other VOCs in numerous samples from water mains, hydrants, and service connections. Many of the benzene detections exceeded regulatory levels. The Paradise Irrigation District (PID) issued a "Do Not Drink/Do Not Boil" water advisory that was not lifted for standing homes until May 2020.[2,3]

Two water utilities were affected by the Camp Fire: PID and the Del Oro Water Company (DOWC) (Figure 1). Drinking water in the Town of Paradise is supplied by PID from a reservoir and treatment plant just north of the town. Smaller surrounding areas are supplied by noncontiguous districts of DOWC, with Paradise Pines and Magalia on groundwater systems to the north, Lime Saddle on surface water to the south, and Buzztail on a groundwater well to the west. A small
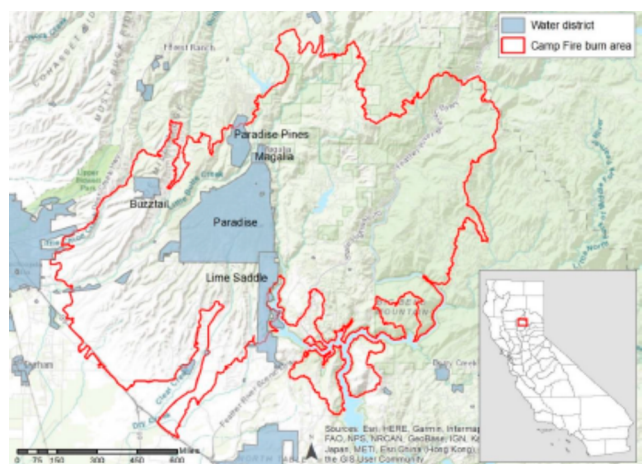
Figure 1. Camp Fire burn area and drinking water systems around Paradise, California. The fire burn area is outlined in red, and the water system service areas are shown in blue. Created by C.C. from refs 4−6.

number of homes that survived the Camp Fire had private wells.

Prior research has reported water contamination after fires from heavy metals, per- and polyfluoro-alkyl substances (PFASs), and microbes.[7−9] VOC contamination after fires is a newly identified issue.[10] The absence of VOCs at the sources and treatment plants of all affected water systems made it clear that the contaminants were being introduced within the distribution system. A recent analysis suggests that burn severity, as measured by the density of damaged structures, is correlated with the probability of VOC contamination exceeding maximum contaminant levels (MCLs).[11] Our project was designed to test for VOCs and conduct nontargeted testing at the tap in standing homes after the Camp Fire in order to characterize potential risk to inhabitants and sources of contaminants. We also analyzed patterns of contamination within the PID system to aid in the interpretation of our tap water findings.

METHODS

Analysis of Paradise Irrigation District Data. To provide background and context for tap water testing, we analyzed VOC testing data from the Paradise Irrigation District. We did not do a full analysis of data from the Del Oro Water Company because our tap water testing did not identify VOCs other than disinfection byproducts in homes in that system and because there was far less data and fewer detections from that system.

PID tested most of its water system starting in December of 2018 and published water quality testing results over a period of nearly 18 months (https://pidwater.com/recovery). Contaminant concentration, compliance status, date, and sampling location were reported for each sample. For service line samples, PID reported whether the service line was connected to a vacant lot, standing structure, or destroyed structure. Water quality advisories for each service connection were lifted once the test results met California standards.

We obtained a downloadable data file from PID of all sampling results over a 17 month period from December 2018 through May 2020. We analyzed the results to explore the VOC concentrations and the extent of contamination over time and across the PID service area. Due to the relatively high detection frequency and concentrations of benzene and methylene chloride (MeCl; also known as dichloromethane), the analysis focused on these chemicals. For locations that were sampled multiple times, the maximum detected levels were used (almost always the first sample for that location). Geographic Information Systems (GIS) mapping and spatial analysis of the service line sample locations were conducted to identify any trends that could further explain possible contamination sources. Sample locations with benzene or MeCl detections were compared to locations without these detections to examine potential differences in spatial intensity using a kernel-based estimator approach[12] and differences in clustering using the K-function.[13,14]

Tap Water Sampling. The tap water sampling strategy aimed to collect samples from 10% of the approximately 1700 homes still standing within the burn zone of the Camp Fire. Because both PID and DOWC reported some benzene detections after the fire, all standing homes in the burn zone served by either water utility were eligible. Homes on private wells were excluded. Our study was reviewed and approved by the Institutional Review Board of the Public Health Institute (IRB# I19-020).

We invited people with standing homes in the fire zone to sign up for the study at a community meeting in September 2019 that was attended by over 100 local residents. We also posted flyers at local businesses, conducted outreach through social media, and email outreach by local organizations, with email and a phone number to sign up for the study. Stories in the local newspaper about the study also encouraged residents to participate. Additional recruitment was done by word-of-mouth and door-to-door in the community. All potential participants that met the inclusion criteria were screened to ensure they were served by water from one of the utilities. Homes that had private water tanks with trucked-in water were excluded, as were homes with point-of-entry multistep filtration systems. Homes with point-of-use carbon filtration were eligible for inclusion because of the potential for saturation. Participants were instructed not to use their kitchen tap for a minimum of 12 h prior to sample collection.

Sampling teams visited 136 homes in October or November of 2019 to obtain written participant informed consent, administer a questionnaire, and collect tap water samples for analysis using EPA Method 524.2, the same VOC analytic method used by PID. Study personnel also collected information about the type of residential structure; the age of the home; whether the home was occupied; types of water pipes; distance from the service connection to the home; degree of fire damage of the home, yard, water meter, and outbuildings; and duration of water stagnation prior to sample collection. Details of the sample collection and analysis are provided in the Supporting Information.

Due to the relatively high detection frequency and concentrations of MeCl, the analysis of the tap water sampling data focused on this chemical. Cross tabulations of observed household factors with detections and concentrations of MeCl were constructed, and p-values from the χ^2 were calculated to assess statistical significance. The MeCl concentrations were highly skewed and log transformations failed to normalize the data distribution (Wilk−Shapiro p-value > 0.20). Therefore, nonparametric ANOVA was used to evaluate whether the median MeCl concentrations differed by potential predictive factors, using the Kruskall−Wallis statistic to assess statistical

Table 1. Distribution of Benzene in Paradise Irrigation District Water Samples Collected December 2018−May 2020 (N = 5056)

type	samples N	detections N	%	over MCL (1 μg/L) %	concentration (μg/L) mean	std dev	median	min	max
main line	2391	45	2	1	4.25	5.27	2.4	0.6	27
appurtenance	448	32	7	6	5.61	7.41	2.2	0.5	29.7
service line: standing structure	1569	35	2	1	8.58	19.23	1.2	0.5	93
service line: destroyed structure	622	183	29	21	26.44	94.36	2.4	0.5	923
all	5056[a]	295	6	4	18.97	75.26	2.3	0.5	923

[a]Samples from service lines connected to vacant land or with unknown structure status did not have benzene detections and were excluded (N = 26).

Table 2. Distribution of MeCl in Paradise Irrigation District Water Samples Collected December 2018−May 2020 (N = 5056)

type	samples N	detections N (%) all samples	flagged samples excluded[a]	over MCL (5 μg/L)% all samples	flagged samples excluded[a]	flagged samples excluded[a] mean	median	max	SD
main line	2391	47 (2%)	29 (1%)	6 (0.3%)	2 (0.08%)	2.97	1.2	28.1	5.55
appurtenance	448	14 (3%)	10 (2%)	1 (0.2%)	0	1.38	1.11	2.4	0.81
service line: standing structure	1569	167 (11%)	41 (3%)	68 (4%)	6 (0.4%)	3.53	1.8	26	5.1
service line: destroyed structure	622	96 (15%)	48 (8%)	47 (8%)	18 (3%)	6.22	2.35	34	8.03
service line: unknown structure status	25	4 (16%)	2 (8%)	2 (8%)	0	1.62	1.62	2.6	1.39
all	5056	328 (6%)	130 (3%)	124 (2%)	26 (0.5%)	3.80	1.5	34	6.08

[a]A total of 198 samples collected by PID in June 2019 were flagged for possible contamination because they were collected using a galvanized steel riser.

significance. For these analyses, samples that were below the practical quantitation limit (PQL) were assigned a value equal to the PQL/square root of two. Although we explored the use of multivariable regression models to simultaneously evaluate potential predictors of MeCl detections and concentrations, the high degree of correlation between factors and the relatively small number of MeCl observations precluded our ability to construct models with stable estimates.

Nontargeted Analysis. We sampled tap water at a subset of 10 homes for a larger number of potential contaminants. Five homes selected for nontargeted testing in October were vacant, and the owner reported minimal or no water use since the fire. Five additional homes were selected in November for follow-up nontargeted testing because benzene or MeCl was detected on initial sampling in October. Details of the nontargeted analysis methods are provided in the Supporting Information.

■ RESULTS

Water System Sampling. Within the PID service area, approximately 9800 of 11 000 service connections were destroyed in the fire. Between December 27, 2018 and May 26, 2020, PID conducted 5056 tests at over 2000 locations. They collected 2391 samples in main lines, 2217 samples in service lines, and 448 appurtenance samples from hydrants, wharf heads, and blow-offs. The most frequently detected VOCs were trihalomethanes including chloroform and bromodichloromethane, benzene, MeCl, and xylenes. Three hundred and twenty-six samples were out of compliance, with one or more VOCs—generally benzene or MeCl—detected above the MCL.

About 6% of samples collected by PID had detectable benzene with a median concentration of 2.3 μg/L and a maximum of 923 μg/L. The distributions of benzene and MeCl are summarized in Tables 1 and 2, respectively. The benzene median concentrations were 2.4 μg/L in main lines

and 2.2 μg/L in hydrants (i.e., appurtenance). The median concentration of benzene in service line samples from destroyed structures was 2.4 μg/L, compared to 1.2 μg/L in service line samples from standing structures. A majority of benzene detections (74%) were found in service lines, as well as about 70% of detections exceeding the MCL. Service line samples collected at destroyed structures had a much higher proportion of benzene detections above the MCL (21%) compared to samples collected at standing structures (1%) (Table 1). The distribution of service line samples also showed a higher proportion of benzene detections above the MCL during the first 6 months of sampling (Figure 2).
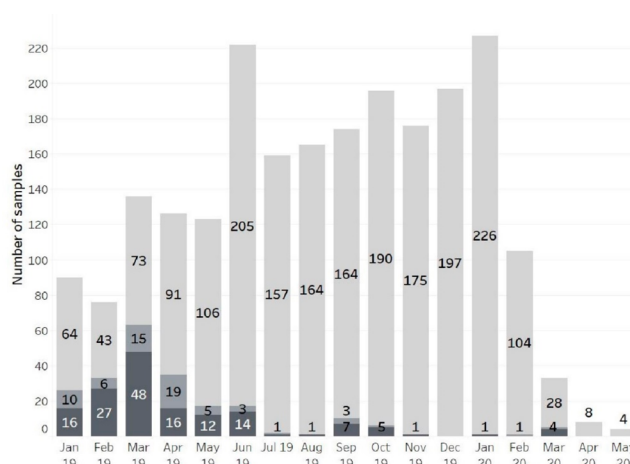

Figure 2. Benzene detections in service lines in the PID service area by sampling date (December 2018−May 2020). Sample results displayed by status from lightest to darkest gray: no benzene detection (ND), benzene detected under the maximum contaminant level (MCL), and benzene detected above the MCL.

Table 3. Distribution of Chemicals Detected in Tap Water Samples Collected October−November 2019 from the Fire and Water Study Homes (N = 136)

chemical	detections			concentration (μg/L)[a]				
	MDL (μg/L)	N	%	mean	std dev	median	min	max
bromodichloromethane	0.20	96	71	2.74	1.04	2.80	0.26	6.80
benzene	0.11	2	1	0.23	0.09	0.23	0.16	0.29
bromoform	0.46	6	4	1.72	0.15	1.65	1.60	1.90
chlorodibromomethane	0.22	7	5	1.56	1.34	0.83	0.52	3.60
chloroform	0.14	106	78	31.66	14.68	31.00	0.14	67.00
methylene chloride	0.21	26	19	1.79	2.53	0.62	0.48	9.20
methyl ethyl ketone	3.3	2	1	34.00	7.07	34.00	29.00	39.00
methyl *tert*-butyl ether	0.14	1	1	0.67		0.67	0.67	0.67
tetrahydrofuran	5.2	3	2	1201.67	1580.21	570.00	35.00	3000.00
trichloroethene	0.19	1	1	0.49		0.49	0.49	0.49
trihalomethanes, total	0.97	109	80	33.47	16.20	33.00	1.20	71.00
o-xylene	0.13	3	2	0.36	0.06	0.39	0.30	0.40
xylenes, total	0.47	2	1	0.60	0	0.60	0.60	0.60

[a]Distribution among samples with detects.

MeCl was reported in 328 samples (6%) at a median concentration of 3.2 μg/L (maximum = 34 μg/L) (Table 2). About 81% of these detections (n = 267) were in service lines to homes, with 117 above the MCL (5%). One hundred and ninety-eight of the total detections (176 from service lines) were flagged by PID as questionable because they were collected using a galvanized steel riser attached to the service connection. PID hypothesized that MeCl might be formed as the water passed through the sampling riser, due to the potential reaction of disinfection byproducts in the water with zinc or iron in the galvanized riser. Excluding the questionable detections, there were 29 MeCl detections in main lines with 2 over the MCL and 91 MeCl detections in service lines with 24 over the MCL. MeCl was detected in 13 field blanks, 1 trip blank, and 5 equipment blanks at generally low concentrations with no MCL exceedances.

Overall, service line samples collected at destroyed structures had twice the rate of MeCl detections above the MCL (8%) compared to samples collected at standing structures (4%), and the median concentration of MeCl in samples from destroyed structures was 2.35 μg/L compared to 1.8 μg/L from standing structures. The pipe material for service lines was not a significant predictor for MeCl detection levels in this sample (p = 0.43, and p = 0.11 with flagged samples excluded), although the pipe material was not reported for many samples. Unlike with benzene, the MeCl detections and MCL exceedances did not decline over time (data not shown).

Over the sampling period, MeCl was detected at 260 service line locations (92 locations with exclusions), benzene was detected at 170 locations, and benzene and MeCl were both detected at 37 locations. Service line locations where benzene was detected above the MCL were more likely to also contain MeCl at detectable concentrations, compared to service lines where benzene was not detected above the MCL (25 vs 12%, p < 0.01). When samples collected through galvanized risers were excluded, the association between benzene and MeCl detections remained significant overall (15 vs 4%, p < 0.01) and for service lines to standing structures (42 vs 11%, p < 0.01) but not for service lines to destroyed structures (22 vs 17%, p = 0.2).

The maps of the MeCl detections showed no clear spatial pattern in detections, MCL exceedances, or apparent association with destroyed structures compared to standing structures (data not shown). However, benzene contamination in service lines was significantly clustered in certain areas of PID's distribution system. A spatial comparison of locations where benzene was analyzed showed a higher intensity of benzene detections in the eastern sections of the town, especially the northeast and southeast corners of the service area (Figure S1). The areas where the number of benzene detections was higher than expected were compared to gas station locations, but no spatial association was observed (data not shown).

Tap Water Sampling. We collected tap water samples at 136 standing homes in October and November 2019. One hundred and eight participating homes were from the PID service area (representing about 9% of standing homes in Paradise), and 28 were from DOWC service areas (representing about 6% of standing homes in those areas). Twenty-two samples had no detected VOCs, of which half were from DOWC groundwater-supplied systems and 10 were from PID homes with private water filtration systems. Water filtration was also present in 15% of the 114 homes with at least one VOC detected.

The most commonly detected VOCs were disinfection byproducts: Total trihalomethanes (TTHMs) were detected in 80% of homes at a median concentration of 33 μg/L (maximum = 71 μg/L). The MCL for TTHMs is 80 μg/L. The most frequently detected THMs were chloroform (78%) and bromodichloromethane (71%) (Table 3). These two THMs almost always co-occurred. Chlorodibromomethane (5%) and bromoform (4%) were detected much less frequently. MCLs have not been established for individual THMs.

Benzene was detected in only 2 samples (1%), both within the PID service area, at concentrations well below the MCL. Both homes were resampled one month later (November 2019) and no benzene was detected. MeCl was detected in 26 samples (19%), at concentrations ranging from just above the PQL to 9.2 μg/L. Four samples had MeCl concentrations above the MCL of 5 μg/L. Tetrahydrofuran was detected in 3 samples (2%), and concentrations ranged as high as 3000 μg/L. No MCL exists for tetrahydrofuran, but 2 samples were above the Michigan guideline value of 350 μg/L.[15] Other VOCs were detected only at trace concentrations in small

Table 4. Methylene Chloride Detections, Stagnation Time, and Pipe Composition

	all		not detected		detected		
characteristic	N	%	N	%	N	%	p-value[a]
all homes	136	100	110	100	26	100	
vacant home							<0.01
yes	29	21	18	16	11	42	
no	107	79	92	84	15	58	
stagnation time (hours)							0.04[b]
3−12 h	27	20	24	22	3	12	
13−24 h	64	47	54	49	10	38	
25−48 h	7	5	7	6	0	0	
72+ h	38	28	25	23	13	50	
type of pipes in the home[c]							
galvanized iron	86	63	68	62	18	69	0.48
copper	97	71	80	73	17	65	0.46
polyvinyl chloride (PVC)	62	46	51	46	11	42	0.71
high density polyethylene (HDPE)	17	13	12	11	5	19	0.32[b]
cross-linked polyethylene (PEX)	4	3	3	3	1	4	0.58[b]
water meter distance (ft)[d]							<0.01[b]
<50 ft	32	24	31	28	1	4	
50−74 ft	34	25	24	22	10	38	
75−120 ft	30	22	28	25	2	8	
>120 ft	33	24	24	22	9	35	
missing/unknown	7	5	3	3	4	15	
water meter distance and type of pipes							<0.01[b]
<75 ft and galvanized iron	46	34	38	35	8	31	
<75 ft and no galvanized iron	20	15	17	15	3	12	
≥75 ft and galvanized iron	36	26	29	26	7	27	
≥75 ft and no galvanized iron	27	20	23	21	4	15	
missing/unknown	7	5	3	3	4	15	
damage to home							0.23
no fire damage	112	82	92	84	20	77	
fire damage	20	15	16	15	4	15	
missing/unknown	4	3	2	2	2	8	
number of outdoor structures on service line burned or damaged							<0.01[b]
none	66	49	58	53	8	31	
one or more	57	42	41	37	16	62	
missing/unknown	13	10	11	10	2	8	

[a]Based on Pearson χ^2, except where noted. [b]Based on Fisher exact. [c]Not mutually exclusive. [d]Distance from house to water meter.

numbers of samples. All detections of benzene, MeCl, and tetrahydrofuran were from the PID system; none of these contaminants were detected in any of the districts of the Del Oro Water Company.

We conducted additional analysis to explore the MeCl detections because these were more frequent than anticipated, and some samples had concentrations above the MCL. The cross-tabulations of MeCl detections with a number of potential factors are presented in Table 4. Homes with detectable levels of MeCl were more likely to be vacant (42 vs 16%, $p < 0.01$) and to have longer stagnation periods (50 vs 23% ≥ 72 h, $p = 0.04$). Regardless of stagnation time, MeCl detections were twice as likely in homes where at least one other outdoor structure on the same water service line burned than in homes where no other structure on the service line burned (62 vs 31%, $p < 0.01$). The frequency of MeCl detections was also associated with the distance between the service connection and the home such that a higher percentage of detections were found among homes situated at distances greater than 120 feet compared to those within 50 feet (35 vs 4%, $p < 0.01$).

Although the median level of MeCl did not statistically differ between homes with and without galvanized iron pipes (median = 0.75 and 0.56 μg/L, respectively; $p = 0.30$), the homes with iron pipes had many more outliers in the high range (Figure 3). Among the homes with iron pipes, 14% had concentrations of MeCl above the measured median concentration of 0.62 μg/L, whereas no homes without iron pipes had MeCl above that level. To investigate the hypothesis that bromodichloromethane (BDCM) and chloroform may be debrominated in the presence of zinc or iron to generate MeCl, we examined the sum of BDCM and chloroform concentrations compared to MeCl concentrations in the water (Figure 4). Overall, the sum of BDCM and chloroform was inversely correlated with MeCl ($r = -0.43$, $p = 0.03$). The inverse correlation was stronger when only homes with iron pipes were examined ($r = -0.56$, $p = 0.02$) and was nonsignificant in homes without iron pipes ($r = -0.32$, $p = 0.54$).

Nontargeted Analysis Results. A list of 48 target semivolatile compounds were quantified in samples from the 10 households selected for NTA to provide a quality check on the results and to perform retention index calibration for
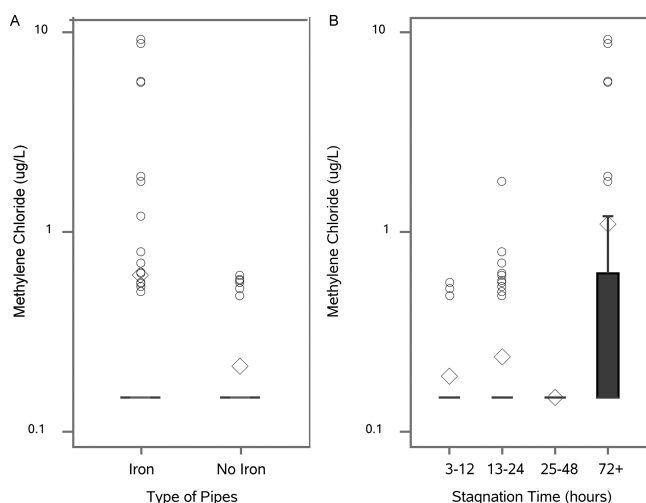
Figure 3. MeCl concentrations in tap water by (A) type of pipes and (B) stagnation time. The diamonds represent the means; open circles are outliers; upper and lower box limits are the first and third quartiles. Note: samples below the practical quantitation limit (PQL) minimum level of detection (MDL) were assigned a value equal to the PQL/square root of two; no respondents reported stagnation times between 49 and 71 h.
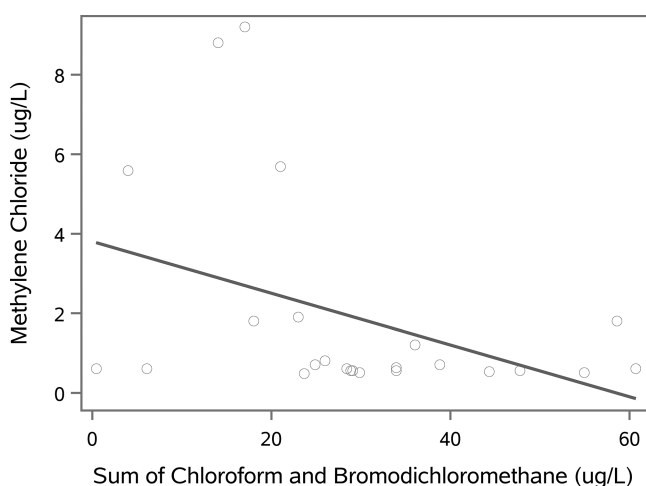

Figure 4. Relationship between methylene chloride concentration and the sum of the concentrations of chloroform and bromodichloromethane in 24 homes with detections of all three chemicals. Note: correlation coefficient = −0.43, $p = 0.02$.

identifying nontargeted compounds. These chemicals included polycyclic aromatic hydrocarbons (PAHs), substituted benzenes, and phthalates; most (33/48) of these compounds were not detected at levels above the method detection limit (MDL) (Table S1). Concentrations of the 15 compounds that exceeded the MDL in one or more samples are reported in Table S2. The most commonly detected compounds, which included two PAHs, three substituted benzenes, a ketone, and a phthalate, are also shown in Figure S2. Two homes in the PID service area (P108 and P113) had particularly elevated levels of phenol (8490−13 650 μg/L) and methyl phenols (*m*- and *p*-cresol) (1059−1648 μg/L). Although these compounds do not have MCLs, phenol concentrations at both homes exceed the U.S. EPA acute health advisory level of 6000 for a 10 kg child. One sample (P108) had 12 compounds that exceeded the MDLs, including naphthalene, fluorene, and

several substituted benzene derivatives (1,2-dichlorobenzene, *o*-cresol, and 2-nitrophenol). Another home (P090) had an elevated level (1738 μg/L) of the widely used plasticizer benzyl butyl phthalate.

An overview of the nontargeted alignment results is presented in Table S3. The total aligned features (1914) were filtered to remove compounds that were not detected in any water samples (e.g., those only in the analytical standard) and to remove peaks that were not significantly higher than found in the blank samples or for which the average signal-to-noise ratio was too low. A total of 509 features met this set of filtering criteria. Tentative identifications were returned for 265 of these. Although the nontargeted method employed here is designed for semivolatile compounds rather than VOCs, there was a strong linear correlation ($r = 0.75$) between the concentrations reported by the target VOC analyses described above and the nontargeted peak heights for bromodichloromethane, which was detected in all 10 samples (Figure S3). Good agreement was observed between the peak areas for a number of our SVOC target compounds and the peak height of the features identified as the relevant target compound (Figure S4) despite the fact that many of the target concentrations were below the formal MDL. A number of the tentatively identified compounds present in numerous samples are readily identified as disinfection byproducts, including trihalomethanes (chlorodibromomethane), haloacetonitriles (HANs, dichloro- and trichloro-) and dichloroacetic acid methyl ester.

The nontargeted data set was further explored in two ways. First, a principal components analysis was applied. For two samples (P108 and P113), this analysis showed that their overall pattern of contaminant concentrations differentiated them from the other household samples (Figure S5). The plot also shows that the chemical signatures of these two samples observed in the nontargeted analysis are reproducible, with a high degree of overlap between the October and November sampling dates and for repeated method blanks and analytical standards. A second way to visualize these multidimensional results is using hierarchical cluster analysis (Figure S6). This manner of viewing the data also emphasizes the significant differences between samples P108 and P113 and the remaining household samples. These two samples had among the highest estimated stagnation times before sampling, which might allow additional time for chemical leaching from adsorbed smoke, deposited ash, or damaged piping materials.

■ DISCUSSION

The contamination of drinking water systems with VOCs following large wildfires has now been documented on several occasions since the phenomenon was first reported in 2017.[7,9] Our study includes a large data set on VOC contamination after the most destructive wildfire in California history, the 2018 Camp Fire. Our analysis includes over 5000 samples collected over a period of 17 months throughout an affected water system, and samples collected at the tap in 136 standing homes in the burn zone 10 months after the fire. Although our tap water testing was limited and may not have been statistically representative—especially in the DOWC service area where we had difficulty recruiting participants—and it was not collected immediately after the fire, the data provide some clues to the sources of the VOC contamination and the time course of the problem.

VOC testing after the Camp Fire showed that, other than disinfection byproducts, benzene and MeCl were the two principal contaminants in the water samples. Our spatial analysis is consistent with that performed by the City of Santa Rosa after the Tubbs Fire in ruling out benzene contamination from leaking aboveground or underground petroleum storage tanks or other point sources of contamination. The fact that concentrations of benzene were highest in service lines to destroyed homes is consistent with the hypothesis that chemical pyrolysis products were pulled into the service lines due to loss of system pressure. The origin of the benzene may include the combustion of residential materials, thermal degradation or pyrolysis of plastic pipes, water meters, and other components of the water system itself, as well as wood smoke.[7,16,17] A prior study on VOCs from crude oil indicates that the adsorption and subsequent release of VOCs varies significantly by type of pipe material, with various types of plastic sequestering and gradually releasing contaminants over weeks or months.[18]

Our analysis of PID data showed that both the concentrations and the detection frequency of benzene declined over the months following the fire; during that time, the water system was being flushed and highly contaminated sections of pipe were replaced. The overall detection frequency of benzene at concentrations above the MCL in service lines serving standing homes was 1%, compared to 21% in service lines serving destroyed homes, suggesting that tap water in standing homes may be relatively less affected. The fact that we did not identify concentrations of benzene near or above the MCL in 136 household tap water samples collected from standing homes 10−11 months after the fire is therefore not entirely surprising. Future investigations collecting samples at the tap in standing homes immediately after a fire could help distinguish between the effect of time and that of standing versus destroyed homes.

Our analysis generally supported prior findings that local burn severity may be associated with higher risk of contamination in service lines.[9] In particular, the cluster of elevated benzene detections in the southeastern portion of the PID service area is associated with a zone of particularly severe fire damage. However, our cluster analysis also identified a higher prevalence of benzene detections in the northeast corner of the PID service area, an area of lower burn severity. This area was the highest of seven pressure zones within the PID system and was the only area to which water was pumped uphill. This zone likely depressurized very quickly once power was lost in the system. An area toward the middle of town that also shows as a cluster in our analysis underwent a service line upgrade in the late-2000s to high-density polyethylene (HDPE) pipes. These findings suggest that burn severity may be just one of several factors determining benzene contamination patterns.

The detection of elevated concentrations of MeCl in a significant number of tap water samples from standing homes was unexpected. Although MeCl is commonly used in laboratories, it is unlikely that it was a laboratory contaminant due to the low or negative results in blanks and the relatively consistent results across study dates and laboratories, including in the PID samples. One prior study reported MeCl as a combustion byproduct of polyvinyl chloride (PVC), suggesting that the detections may be related to smoke from pyrolysis of pipes or other plastic.[14] However, our tap water testing found MeCl, sometimes at levels exceeding the MCL, in samples that did not contain benzene or other markers of combustion. The elevated concentrations of benzene and MeCl in the PID samples were also weakly correlated, raising questions about whether the only source of MeCl was combustion.

MeCl (dichloromethane) could potentially be produced from the dechlorination of chloroform (trichloromethane) or the debromination of bromodichloromethane (BDCM), especially in the presence of iron or zinc in pipes. One laboratory study found that chloroform can be transformed to MeCl within hours under experimental conditions and that MeCl subsequently remains stable for days or longer.[19] The dehalogenation hypothesis is supported by the higher concentrations of MeCl we found in tap water samples with longer stagnation times and longer distances between the tap and the service connection, especially in homes with galvanized iron pipes. The inverse association we found between MeCl concentration and the concentration of chloroform and BDCM, especially in homes with galvanized iron pipes, also supports the hypothesis that these trihalomethanes may be converted to MeCl in the presence of iron and zinc. PID was concerned that a galvanized riser they were using for sample collection was responsible for some of the MeCl detections in their data even though the water may have only been in contact with the galvanized riser for seconds, and they flagged some MeCl detections as potentially unreliable for this reason; however they also found MeCl in samples when the riser was not used. If this hypothesis is correct, MeCl could be produced in the absence of a wildfire, from stagnant disinfected water in iron pipes.

We detected tetrahydrofuran (THF) in three tap water samples in the PID service area. THF was not included in the PID data set. THF is used as a solvent in polymers and resins and is commonly used in PVC adhesives for drinking water pipes. The Safety Data Sheet for the brand of PVC primer and cement used by PID contains 10−25% THF.[20] PID was removing residential water meters and installing "jumper" PVC pipe connections on service lines to standing homes during the time period of our tap water sampling. There is limited information on the health effects of THF. Some *in vivo* bioassays showed evidence of hepatotoxicity, neurotoxicity, and developmental toxicity.[21] One study showed evidence of kidney and liver tumors in both rats and mice, on the basis of which the U.S. EPA concluded that THF shows "suggestive evidence of carcinogenic potential".[17] The International Agency for Research on Cancer classified THF as "possibly carcinogenic to humans" (Group 2B), on the basis of sufficient evidence of carcinogenicity in animals.[22]

■ CONCLUSIONS

The contamination of drinking water systems during wildfire events is a new environmental health challenge. Addressing the root causes of wildland-urban interface extreme fire events (e.g., climate change, forest management) are important components but must be supplemented by resilience measures for water systems. The ability to quickly shut-off sections of water systems that depressurize, coupled with backflow prevention, may reduce contamination from smoke being pulled into service lines and other pipes. Rapid post-fire testing throughout the system, with a focus on initially clearing water mains, followed by service lines to standing homes, is a critical element. Finally, the strategies of flushing pipes that have low levels of contaminants and the replacement of highly contaminated pipes appear to have been effective in the area

impacted by the Camp Fire. Further research to test water that has stagnated in galvanized pipe is needed, especially because the implications may extend beyond the relatively few fire-impacted water systems. MeCl is typically not tested in the distribution system or at the tap, and compliance testing at the water treatment plant would not ensure against chemical transformation within the system. More widespread monitoring for chemicals known to be used in water pipe repair, such as tetrahydrofuran, along with drinking water guidance values, would help ensure public health protection.

■ ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.1c00129.

> Discussions of methods used, figures of Paradise Irrigation District's service boundary and sampled service lateral locations, target semivolatile organic compound concentrations, illustration of the nontarget feature alignment and identification process in MS-DIAL, comparison between nontarget peaks identified as target compounds and the corresponding area counts, principal components analysis, and hierarchical cluster analysis, and tables of semivolatile organic compounds included as targets in the nontarget analysis and summary of the results of each filtering step applied during the nontarget workflow (PDF)

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Notes

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